PATENT SPECIFICATION

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COMPLETE SPECIFICATION.

Improvements in or relating to the Treatment of Edible Fatty Oils and Fats more particularly those Containing Fat-Soluble Vitamins.

We, NATIONAL OIL PRODUCTS COMPANY, a Corporation duly organised and existing under and by virtue of the Laws of the State of New Jersey, United States of America, of Harrison, Hudson County, New Jersey, United States of America, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

This invention relates to improvements in the treatment of edible fatty materials for the purpose of concentrating the unsaponifiable fraction thereof and more particularly to the production of high potency fat-soluble vitamin oils and concentrates having improved taste and odour.

It is common practice in the concentration of vitamin-bearing fatty materials to subject such materials to the action of alkalis to saponify and remove all or part of the fatty substances and thus concentrate the vitamin principles in the unsaponified residue. Such vitamin-bearing materials, notably the fish liver oils, contain substances of undesirable taste and odour, and alkali treatments tend to develop, concentrate and fix these substances in the vitamin-bearing matter in forms very difficult to remove by subsequent treatments.

It has heretofore been discovered that undesirable tastes and odours can be removed from edible fatty materials by contacting such materials with edible gums, sugars, and the like, at temperatures between 100° C. and 200° C. While these processes have proved highly efficacious this operation constitutes an extra step in the refining process and involves application of heat to the sensitive vitamin materials.

It is an object of this invention to minimise or prevent the tendency of alkalis to develop, concentrate and fix substances of undesirable taste and odour in the unsaponified portions of fatty materials treated therewith and to remove such substances when present.

[*Price* 1*s.*]

The above and other objects are achieved in accordance with this invention by mixing a small quantity of a substance hereinafter called the "fixative material", consisting of sugars, sugar esters, ketones or like sugar derivatives and/or edible gums, into a fatty material which is being treated, or one which is to be treated with alkali. The unsaponified portion of the fatty material when separated from the soap and fixative material after the saponification is substantially devoid of the usual characteristic "concentrate" odour and taste, the substances producing odour and taste having been taken up by the fixative material and the further development of these substances prevented thereby. The saponification may be carried out at room or only slightly elevated temperature in accordance with the usual practice in alkali treatment of fatty materials.

Any fat-soluble vitamin or provitamin-containing fatty material having an undesirable taste and odour, or one which develops undesirable taste and odour when treated with alkali, may be treated in accordance with this invention; thus the process of this invention may be applied to fatty materials containing vitamins A, D, E or K, such as, for example, cod liver oil, halibut liver oil, swordfish liver oil, tuna liver oil, shark liver oil, whale liver oil, porpoise liver oil, seal liver oil, sardine oil, wheat germ oil, palm oil and similar oils. The process of this invention is particularly applicable to the concentration of vitamin A and/or D containing oils of fish origin, since treatment of such materials in accordance with the invention produces products far superior to any of those now on the market. Further, this process can also be applied to non-vitamin oils that are to be saponified for the recovery of the unsaponifiable material.

As an odour and taste fixative substance for the process of this invention there may be employed sugars and edible gums. Specific examples of substances falling within this group include, among

others, arabinose, pectin, lactose, galactose, maltose, sorbitol, mannitol, sucrose, glucose, dextrose, xylose and the like; the esters, ketones and like derivatives of the sugars; any edible gum such as, for example, gum tragacanth, gum arabic, gum guaiac, gum mastic, and other gums well known in the art; or any edible commercial substance consisting substantially of one or more of the above materials, such as molasses, corn syrup, malt syrups, honey and pomace. In practice it has been found that the best results are obtained when a sugar or sugar containing fixative is used, particularly blackstrap molasses, honey and sorbitol.

It is advantageous to remove completely air or oxidising gases from the fixative material before employing it in the practice of this invention in order to minimise oxidation of the vitamins; this removal of oxidising gases may be carried out by forming an aqueous slurry of the material, and warming the slurry while bubbling an inert gas there through with thorough agitation until all oxidising gases are completely removed. The slurry thus obtained may be employed directly in the practice of the present invention. Other methods of removing oxidising gases may be employed.

In carrying out the process of the invention, a fat-soluble vitamin-containing oil is mixed with a suitable amount of the fixative material of the type described, and the mixture subjected to treatment with alkali. The amount of fixative material may vary widely, depending to some extent upon the odour and taste of, or latent in, the vitamin-containing oil to be treated; generally, however, an amount between 1% and about 20% of the weight of the vitamin containing oil is suitable.

The manipulative details of the saponification procedure *per se* do not constitute a part of this invention; conveniently, however, the procedure disclosed in the Patent No. 550,845 may be employed in the preparation of the unsaponifiable fraction of fish liver oils. In accordance with the present invention, the fixative material is admixed with the oil prior to or during the alkali addition in the aforementioned processes. The amount of caustic used may vary, but will usually be between about 25% and about 125% of the amount required to saponify completely the saponifiable material in the oil. In the production of the unsaponifiable fraction of an oil the fat should be reacted with alkali. However, where it is desired merely to produce a so-called high potency oil, only a portion of the fat will be removed by saponification.

The process of the present invention may be used in conjunction with other refinement procedures which may precede or follow the present process as far as sequence is concerned. For instance the oil subjected to the present process may be pretreated by the process described in the present applicants' British Patent Specification No. 535,014.

The refined products of the present invention possess very little, if any, of the tastes and odours characteristic of the material from which they are obtained; hence, these products are eminently suitable for a variety of purposes and find particular application in the preparation of vitamin products for human consumption. Further, these products do not have the characteristic bitter "concentrate" taste usually developed during the alkali concentration of vitamin oils.

The exact mechanism whereby the fixative materials remove the objectionable taste and odour is not known; it is believed, however, that the hydroxyl groups in the sugars are converted into aldehyde, carboxyl and keto groups upon contact with the alkali, which groups, in turn, react with the bad-tasting and odoriferous substances in the oil during the saponification step and thus carry them out of the oily phase of the saponification mass. However, the invention is not dependent upon the foregoing or any other particular theory of operation.

The following examples further illustrate the nature of the invention and the manner in which it may be carried into effect, all parts given being by weight.

EXAMPLE I.

200 parts of crude shark liver oil, 100 parts of ethylene dichloride, 6 parts of isopropanol and 7 parts of blackstrap molasses were admixed in an insulated kettle. The mass was agitated while introducing nitrogen gas into the mass from a point at the bottom of the kettle. After the mass has been stirred sufficiently to effect homogeneity throughout, agitation was continued while adding an aqueous 45% KOH solution (15% excess over the amount theoretically required to saponify completely all the saponifiable matter in the oil) at 40° C. to 60° C. Agitation of the mass was continued until an emulsion heavily charged with solvent was formed which did not break or bleed when stirring was discontinued. The mass was allowed to stand overnight in the heat-insulated kettle. The mass was heated to a temperature of 60° C. to 80° C. while gently agitating for a period of one hour until the soap changed from a paste-like mass to separate and individual granular, fluffy and feathery

particles. 500 parts of ethylene dichloride were added with stirring and the mass cooled to room temperature, whereupon the soap particles floated to the top of the liquid. The liquid layer was drawn off and the solvent removed therefrom by distillation under reduced pressure. The soap was washed again with fresh solvent to remove the adsorbed unsaponifiables as before, The resultant removed as before. The resultant unsaponifiable fraction was completely devoid of undesirable characteristic bitter taste and odour.

EXAMPLE II.

200 parts of crude shark liver oil, 100 parts of ethylene dichloride, 6 parts of isopropanol and 6 parts of commercial sorbitol were admixed in an insulated kettle. The mass was agitated while introducing nitrogen gas into the mass from a point at the bottom of the kettle. After the mass had been stirred sufficiently to effect homogeneity throughout, agitation was continued while adding an aqueous 45% KOH solution (15% excess over the amount theoretically required to saponify all the saponifiable matter in the oil) at 40° C. to 60° C. Agitation of the mass was continued until an emulsion heavily charged with solvent was formed which did not break or bleed when stirring was discontinued. The mass was allowed to stand overnight in the heat-insulated kettle. The mass was heated to a temperature of 60° C. to 80° C. while gently agitating for a period of one hour until the soap changed from a paste-like mass to separate and individual granular, fluffy and feathery particles. 500 parts of ethylene dichloride were added with stirring and the mass cooled to room temperature, whereupon the soap particles floated to the top of the liquid. The liquid layer was drawn off and the solvent removed therefrom by distillation under reduced pressure. The soap was washed again with fresh solvent to remove the adsorbed unsaponifiables thereon, and the solvent removed as before. The resultant concentrate was completely devoid of undesirable fishy taste and odour and of any characteristic bitter "concentrate" taste.

EXAMPLE III.

20 parts of adsorptive carbon and 1800 parts of ethylene dichloride were admixed in an open vessel. The mass was moderately agitated for 5 minutes to remove completely oxidising gases therefrom, after which 200 parts of shark liver oil were added slowly. The stirring was continued for 30 minutes. 20 parts of a filtration promoting substance were added and the mass filtered. The residue was washed 5 times with 10-part portions of ethylene dichloride. The filtrate and washings were combined and the solvent removed by vacuum distillation in the presence of nitrogen gas. The resultant oil was treated by the process of Example 1, using the oil in place of the crude shark liver oil employed therein. The resulting product was bland tasting and had no objectionable odour.

EXAMPLE IV.

200 parts of crude shark liver oil were admixed with 10 parts of clover honey and the mixture heated to 150° C. and maintained at this temperature for 10 minutes in a nitrogen atmosphere and under 10 mm. pressure. At the end of this time, the mass was allowed to cool and thereafter treated according to the process of Example 1, using the same in place of the crude shark liver oil in said example. The product was devoid of fish, bitter or other disagreeable tastes and odours.

While the foregoing specific examples are directed to the preparation of vitamin concentrates substantially devoid of fatty material, it is to be understood that high potency oils may also be produced whereby the high vitamin end-product will contain a portion of the original triglycerides. Moreover, it is not necessary according to this invention that saponification, whether complete or partial, be carried out in the presence of an organic solvent. As aforementioned the salient feature of the invention resides in the step of saponifying fatty materials in the presence of a fixative material of the type herein disclosed.

It will be evident from the above description that this invention provides a new and effective method of preparing substantially odourless and tasteless vitamin-containing materials from fat-soluble vitamin-containing materials having objectionable tastes and odours and is therefore of great utility in the preparation of vitamin compositions, especially for human and animal consumption.

Having now particularly described and ascertained the nature of our said invention and in what manner the same is to be performed, we declare that what we claim is :—

1. A process for the treatment of edible fatty oils and fats containing unsaponifiable matter to concentrate the unsaponifiable fraction thereof which comprises saponifying the fatty material in the presence of a sugar, sugar ester, ketone or like sugar derivative or edible gum, removing the resulting soap and recovering the unsaponifiable products.

2. A process as claimed in Claim 1

wherein the edible oil treated is a fat-soluble vitamin-containing oil, e.g. a fish liver oil.

3. A process as claimed in Claim 2 wherein the vitamin potency is increased by separating the vitamin enriched fraction from the resulting soap and fixative material by solvent extraction.

4. A process as claimed in Claim 3 wherein the saponification step is carried to completion for the purpose of recovering the unsaponifiable fraction.

5. A process for treating edible fatty oils and fats including fat-soluble vitamin-containing oils substantially as described in any one of the specific examples hereinbefore set forth.

6. Edible products from fatty oils and fats including fat-soluble vitamin-containing oils and concentrates whenever produced by the process as claimed in any one of the preceding Claims.

Dated this 20th day of July, 1942.
KILBURN & STRODE,
Agents for the Applicants.

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